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13. ABSTRACT *(Maximum 200 words)*

We developed new approaches for preparing ultrathin film composite membranes based on the anionically/electronically conductive polymers that were of interest to this research effort. Of particular interest, we developed methods for coating microporous hollow fibers with thin films of such polymers. This is important because hollow fiber supports provide the highest active surface area per unit volume of any support material. High surface area insures high permeant (e.g., anion, molecule or electron) flux. In addition, we showed that these anion/electron-conductive polymers can be used to drive electron/ion transfer reactions across membranes containing these polymers.

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Contract AFOSR-AASERT-F49620-93-1-0343

FINAL TECHNICAL REPORT

for Period 1 June 1993 to 31 May 1996

"ANIONICALLY-CONDUCTIVE ULTRATHIN FILM COMPOSITE MEMBRANES"

by

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30 July 1996

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FINAL TECHNICAL REPORT

This is the final technical report for the AFOSR-AASERT-F49620-93-1-0343 sponsored research project, "Anionically-Conductive Ultrathin Film Composite Membranes." This report summarizes progress made during the period June 1, 1993, to May 31, 1996.

Objectives:

The objective of this research effort was to explore ion, mass and electron transfer in anionically-conductive ultrathin film composite membranes. These ultrathin film composite membranes consisted of a microporous support material coated with an ultrathin skin of a selectively permeable polymer. The polymers investigated are known collectively as "electronically conductive polymers." Examples studied in this work include polypyrrole, polyaniline and poly(N-methylpyrrole). These are electroactive polymers with one redox state being a polycation. This allows these materials to be anion conductors. The ultrathin film composite approach allows for high rates of ion (and mass and electron) transport due to the ultrathin nature of the polymer film.

Status of Effort:

Unfortunately, this is a final report. This is due to the fact that the program under which this work was sponsored (headed by Dr. John Wilkes) was terminated. As a result, work in this area has stopped. However, this was a very productive research program, resulting in 16 publications.

Accomplishments/New Findings:

The work is presented in detail in the 16 publications that have resulted from the research program. Hence, a detailed review is not needed in this report. Suffice it to say, however, that we developed new approaches for preparing ultrathin film composite membranes based on the anionically/electronically conductive polymers that were of

interest to this research effort. Of particular interest, we developed methods for coating microporous hollow fibers with thin films of such polymers. This is important because hollow fiber supports provide the highest active surface area per unit volume of any support material. High surface area insures high permeant (e.g., anion, molecule or electron) flux.

In addition, we showed that these anion/electron-conductive polymers can be used to drive electron/ion transfer reactions across membranes containing these polymers. These membrane, in a sense, mimic biological membranes that allow for simultaneous ion and electron transfer. In our case the transport processes were driven by the free energy change of the electron transfer process. That is, an electron donor was placed on one side of the membrane and an electron acceptor was placed on the other. The transport process (which entail both electron and ion transport across the membrane) is driven by the free-energy change of the donor/acceptor reaction.

The other important point to note is that we have shown that these ion/electron-transport polymers (the electronically conductive polymers) can show exceptional gas-transport selectivity. In particular, we have been interested in O_2 transport selectivity in membranes. Membranes which selectively transport O_2 (in particular with respect to N_2) have numerous commercial and technological applications. These include possible uses in fuel cells for enrichment of the O_2 in the feed-gas stream and uses in industrial gas separations. We showed as part of this work that the electronically conductive polymer polyaniline can have an O_2 vs. N_2 transport selectivity coefficient as high as 15. This means that an ultrathin film composite membrane based on polyaniline shows a 15 times higher flux for O_2 vs. N_2 when both molecules are present on the feed side of the membrane at the same partial pressure. This is one of the highest $_2$ vs. N_2 selectivity coefficients to be described in the literature to date.

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Publications:

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Interactions: Lectures presented:

1 "Nanomaterials: A Membrane-Based Synthetic Approach," Texas Instruments, Dallas, Texas, May 9, 1996.

2 "Template Synthesis of Polymeric Nanostructures," Materials Research Society, San Francisco, California, April 10, 1996.

3 "Metal Nanotubule Membranes--Selective Ion Transport and Molecule Filtration," ACS meeting, New Orleans, Louisiana, March 25, 1996.

4 "Electrochemistry--Nanoelectrode Ensembles," University of Venice, Venice, Italy, March 7, 1996.

5 "Metal Nanotubule Membranes and Electrodes," Pittsburgh Conference on Analytical Chemistry, Chicago, Illinois, March 4, 1996.

6 "Electrochemistry at Ensembles of Nanoscopic Electrodes," Tokyo University of Agriculture and Technology, Tokyo, Japan, February 7, 1996.

7 "Nanomaterials and Nanoelectrochemistry," Tsukuba Science Center, Tsukuba, Japan, February 3, 1996.

8 "Nanomaterials and Nanoelectrochemistry," Hokkaido University, Sapporo, Japan, February 1, 1996.

9 "Nanomaterials and Nanoelectrochemistry," Osaka University, Osaka, Japan, January 30, 1996.

10 "Nanomaterials--A Membrane Based Synthetic Approach," Lawrence Berkeley Laboratory, Berkeley, California, January 11, 1996.

11 "Nanomaterials--A Membrane Based Synthetic Approach," American Institute of Physics, Dearborn, Michigan, October 24, 1995.

12 "Nanomaterials and Nanoelectrochemistry," Indiana University, Bloomington, Indiana, October 13, 1995.

13 "Metal Nanotubule Membranes with Electrochemically Switchable Ion-Transport Selectivity," ACS Regional Meeting, Chicago, Illinois, August 22, 1995.

14 "Membrane Synthesis of Nanomaterials," Gordon Conference on Membranes, Plymouth State College, NH, July 26, 1995.

15 "Membrane-Based Chemical Separations--New Materials and New Concepts," University of Cincinnati, Cincinnati, Ohio, June 30, 1995.

16 "Electrochemistry at Nanometal-Containing Membranes--Nanodisk and Nanotubule Electrodes," ACS Regional Meeting, Park City, Utah, June 15, 1995.

17. "Membrane-Based Separations Using Electronically Conductive Polymers," North American Membrane Society meeting, Portland, Oregon, May 21-24, 1995.

18. "Electrochemistry at Ensembles of Nanoscopic Electrodes," Tohoku University, Sendai, Japan, April 13, 1995.

19. "Electrochemistry at Ensembles of Nanoscopic Electrodes,"Kyoto University, Kyoto, Japan, April 12, 1995.

20. "Nanomaterials - A Membrane-Based Synthetic Approach,"Ciba-Geigy, Kobe, Japan, April 11, 1995.

21. "Electrochemistry at Ensembles of Nanoscopic Electrodes, "Osaka University, Osaka, Japan, April 10, 1995.

22. "Electrochemistry at Ensembles of Nanoscopic Electrodes,"Tokyo University of Agriculture and Technology, Tokyo, Japan, April 7, 1995.

23. "Nanomaterials - A Membrane-Based Synthetic Approach," Showa Denco, Inc. Chiba, Japan, April 6, 1995.

24. "Electrochemistry at Ensembles of Nanoscopic Electrodes," Japanese Electrochemical Society annual meeting, Tokyo, Japan, April 4, 1995.

25. "Electrochemistry at Nanometal-Containing Membranes--Nanodisk and Nanotubule Electrodes," University of Rome, Rome, Italy, March 20, 1995.

26. "Electrochemistry at Nanometal-Containing Membranes--Nanodisk and Nanotubule Electrodes," University of Venice, Venice, Italy, March 17, 1995.

27. "Electrochemistry of Cephalosporin C Derivatives," Antibioticos, Turin, Italy, March 14, 1995.

28. "Electrochemistry at Ensembles of Nanoelectrodes," Pittsburgh Conference, New Orleans, Louisiana, March 6-7, 1995.

29. "Electrochemical and Optical Investigations of Nanometal Arrays," ONR Contractors' Meeting, Los Angeles, California, January 13-15, 1995.

30. "Electrochemistry at Ensembles of Nanoelectrodes," Eastern Analytical Symposium, Somerset, New Jersey, November 14, 1994.

31. "Nanomaterials--A Membrane-Based Synthetic Approach," Second NSF Materials Chemistry Workshop, St. Louis, Missouri, October 13-16, 1994.

32. "Materials Science Aspects of Bioelectrochemistry," International Society of Electrochemists, Porto, Portugal, September 2, 1994.

33. "Bioencapsulation in Conductive Polymer Nanocapsules," Abbott Laboratoeries, Chicago, Illinois, July 20, 1994.

34. "Electrochemistry and Electro-organic-chemistry," Schering-Plough Research Institute, Union, New Jersey, May 13, 1994.

35. "Conductive Polymer Microstructures--Synthesis and Applications," National ACS meeting, San Diego, California, March 14, 1994.

36. "Nanomaterials--A Membrane Based Approach," University of Utah, Salt Lake City, Utah, March 3, 1994.

37. "Nanomaterials--A Membrane Based Approach," Utah State University, Logan, Utah, March 2, 1994.

38. "Nanomaterials--A Membrane Based Approach," University of Puerto Rico, Rio Piedras, Puerto Rico, February 14, 1994.

39. "Nanochemistry and Nanomaterials," Southwest Analytical Professors' meeting, Fresno, California, January 22, 1994.

40. "Fabrication and Electrochemical Characterization of Ensembles of Nano-Disk Electrodes with Disk Diameters as Small as 100 Å," Gordon Conference on Electrochemistry, Ventura, California, January 19, 1994.

41. "Gas Transport Properties of Electronically Conductive Polymers and Related Materials," Dow Chemical, Michigan, November 12, 1993.

42. "Template Synthesis of Electronically Conductive Polymers," International Society of Electrochemistry, Berlin, GERMANY, September 5-10, 1993.

43. "Nanomaterials," National Renewable Energy Laboratory, Golden, Colorado, August 18, 1993.

44. "Membrane-based Separations with Electronically Conductive Polymers," Gordon Conference on Membranes: Materials and Processes, Plymouth State College, New Hampshire, August 1-6, 1993.

45. "Nanochemistry--A Membrane-Based Approach," University of Cincinnati, Cincinnati, Ohio, July 29, 1993.